NITROGEN ISOTOPES IN PALEOCLIMATE RESEARCH

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NITROGEN ISOTOPES

Introduction

Nitrogen, element number five in the Periodic Table, is a limiting nutrient to primary production (i.e., plant growth) on the continents and in the ocean (Dugdale and Goering, 1967). Phytoplankton productivity is generally high where fixed (i.e., soluble) nitrogen concentrations are elevated and low where they are diminished. Because primary productivity influences climate, via the uptake of atmospheric carbon dioxide, and is the precursor to petroleum deposits it is important to understand nitrogen cycling in the environment. The stable isotopes of nitrogen, ^{14}N and ^{15}N, representing, respectively, 99.63% and 0.37% of nitrogen atoms in the solar system, provide a powerful tool for elucidating the processes that transfer nitrogen between reservoirs because many of them cause large isotopic fractionations that can be measured with a mass spectrometer.

The Global Nitrogen Cycle

The largest reservoir of nitrogen on the planet is rocks, which contain 1.9 x 10^{11} Tg (10^{12} g) of nitrogen (Wada and Hattori, 1990). Nitrogen in rocks is not very reactive and therefore has a very long residence time. The largest available pool of nitrogen is atmospheric dinitrogen gas (N_2), consisting of 3.9 x 10^9 Tg N (Wada and Hattori, 1990). For comparison, the total amount of nitrogen contained in all plants and animals on the continents is 1.5 x 10^4 Tg N and in the ocean is 4.7 x 10^2 Tg N, both very much smaller than the reservoir of nitrogen in the atmosphere. While some specialized microbes are able to convert N_2 gas into ammonia (NH_3), the biologically useful form of nitrogen, by a process called nitrogen fixation most primary producers require fixed nitrogen in the form of nitrate (NO_3^-) or ammonium (NH_4^+). The pool of nitrate in the ocean is 5.7 x 10^5 Tg N and 7 x 10^3 Tg N, respectively (Wada and Hattori, 1990).

The marine nitrogen cycle is complex and not well understood (Codispoti, 1995). Current estimates indicate that the total of all oceanic sinks for nitrogen are larger than combined sources by 75% (Codispoti and Christensen, 1985) but uncertainties of a factor of two to four exist regarding the magnitude of each. Sources of fixed nitrogen to the ocean are (i) nitrogen fixation (30-130 Tg N/yr), (ii) atmospheric deposition (30-83 Tg N/yr), and (iii) river runoff (13-24 Tg N/yr) (Wada and Hattori, 1990). Sinks of nitrogen in the ocean are (i) microbial denitrification, the conversion of nitrate to N_2 gas with its subsequent loss to the atmosphere (25-180 Tg N/yr), (ii) burial in marine sediments (20 Tg N/yr), and (iii) exports of organic nitrogen to the continents via fish catches, guano deposition, and atmospheric transport (10-20 Tg N/yr) (Codispoti and Christensen, 1985).

While the combined exports of nitrogen substantially exceed combined imports in the above tally, recent studies indicate that nitrogen fixation rates may have been drastically underestimated by a factor of two or more (Gruber and Sarmiento, 1997; Karl et al., 1997; Zehr et al., 2001). So the marine nitrogen cycle may be approximately in balance. Nevertheless future studies are needed to better constrain the sources and sinks and sinks of nitrogen in the ocean.

Nitrogen Isotope Ratios

Nitrogen isotopic ratios are typically measured on gaseous nitrogen (N_2 or N_2O) in a dual-inlet mass spectrometer. Very high precision, on the order of 0.01% or better, is obtainable using this technique. The isotope ratio of a sample is reported relative to that of a reference standard and reported in delta notation in units of per mil (‰), where one per mil is one-tenth of one percent, or one part per thousand, according to Equation 1:

$$\delta^{15}N = (^{15}N/^{14}N_{sample}/^{15}N/^{14}N_{standard}) - 1 * 1000\ ‰ \qquad (1)$$

Atmospheric nitrogen (N_2) is the reference standard for nitrogen isotopic analyses and has a $\delta^{15}N$ value defined as 0 ‰.

The biologically-mediated reduction reactions that convert nitrogen from nitrate (NO_3^-, +5 oxidation state) to nitrite (NO_2^-, +3) to nitrous oxide (N_2O, +1), to nitrogen gas (N_2, 0), and to ammonia (NH_3, -3) are faster for ^{14}N than for ^{15}N as a result of higher vibrational frequency of bonding to ^{14}N than to ^{15}N (Owens, 1987). This results in products that are ^{15}N-depleted (i.e., have a lower $^{15}N/^{14}N$ ratio and lower $\delta^{15}N$) relative to the substrate. If the substrate reservoir is either closed or has inputs and outputs that are slow relative to one of the reduction processes then the reservoir will become enriched in ^{15}N. An example is the oxygen-depleted sub-surface water of the eastern tropical Pacific Ocean where high rates of denitrification cause large ^{15}N enrichments of the nitrate pool on the order of 1% (or 10‰) (Cline and Kaplan, 1975). Denitrification in low-oxygen regions of the ocean, such as the eastern tropical Pacific and the Arabian Sea cause the $\delta^{15}N$ value of the ocean nitrate reservoir to be high (~ 5 ‰) relative to the atmosphere and to terrestrial nitrogen (Sigman et al., 1999; Wada et al., 1975).

During the reduction of N_2 to NH_3 by nitrogen fixing bacteria in the ocean atmospheric nitrogen ($\delta^{15}N = 0$ ‰), which is already isotopically-depleted relative to ocean fixed nitrogen, is further depleted, resulting in organic nitrogen with a $\delta^{15}N$ value of –2.7 ‰ (c.f., Sachs and Repeta, 1999, and references therein). In regions of the ocean where nitrogen fixation is extensive, such as in the subtropical north Pacific (Karl et al., 1997; Liu et al., 1996) and in the Mediterranean Sea (Sachs and Repeta, 1999), $\delta^{15}N$ values are low in both phytoplankton and fixed nitrogen relative to global ocean average values.

Oxidation reactions that convert ammonia to N_2O, NO_2^- and NO_3^- during nitrification also result in isotopic fractionation (Mariotti et al., 1981; Yoshida et al., 1989).

Diagenetic Alteration of Nitrogen Isotope Ratios

Early diagenetic (i.e., decomposition) reactions in marine sediments can severely alter the isotopic composition of sedimentary organic nitrogen. This is critical to consider when attempting to interpret nitrogen isotopic ratios in whole sediment because the effect of diagenesis can be as large as the primary signal that is sought. For example, the diagenetic overprint of sedimentary nitrogen isotopic values typically ranges from 3-8 ‰ in sediments overlain by well-oxygenated water (Altabet and Francois, 1994; Sachs and Repeta, 1999), while the total range of isotopic variation is typically less than 5 ‰. The problem of diagenetic alteration of sedimentary $\delta^{15}N$ values is less of a concern in sediments overlain by oxygen-depleted water (Altabet et al., 1999; Sachs and Repeta, 1999).

One means of circumventing the issue of diagenesis is to measure nitrogen isotopic ratios on molecular fossils, or “biomarkers”. These molecules have a known source and, if found intact, are unlikely to have been altered isotopically. Chlorophyll and its decomposition products, chlorins, are ideal for this purpose because they are produced by all primary producers and persist in sediments for millions of years (Sachs and Repeta, 1999). Algal culture studies indicate that chlorophyll $\delta^{15}N$ values reflect those of the host alga with a constant isotopic depletion of 5.1 ‰ (Sachs et al., 1999). Methods for purifying chlorins for nitrogen (and carbon) isotopic analysis are described in (Sachs and Repeta, 2000).

Conclusion

Nitrogen isotopic ratios provide a powerful tool for evaluating processes within the nitrogen cycle and for reconstructing changes in the cycling of nitrogen through time. Because multiple nitrogen transformation reactions occur simultaneously in any environment, with some leading to nitrogen isotopic enrichment and some to isotopic depletion of the reservoir of interest, it can be difficult to discern the most important processes. Nitrogen isotopes are therefore most useful in environments where one or more transformation processes can be ruled out.

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Cross-references

Biomarker
Chlorophyll and chlorins
Denitrification
Diagenesis
Geochemistry of sediments
Nitrogen cycle
Nitrogen fixation
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